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Energy Procedia 37 (2013) 961 – 968

Energy Procedia

GHGT-11

Molecular Gate Membrane: Poly(amidoamine) Dendrimer/polymer Hybrid Membrane Modules for CO_2 Capture

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Abstract

Japanese government declared a goal to reduce CO_2 emissions to half of those in 2005 as the objective "Cool Earth 50". One promising means of reducing CO_2 emission is the development of integrated coal gasification combined cycle with CO_2 capture & storage (IGCC-CCS). In the IGCC-CCS process, CO_2 separation membranes will play an important role for reducing CO_2 capture costs. Estimates indicated that the CO_2 capture cost from a pressurized gas stream using a membrane would be 1,500 JPY/ton- CO_2 or less.

We are currently developing CO_2 molecular gate membrane, with the goal of producing a new, high-performance separation membrane modules. In the concept of the molecular gate membrane, the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of H_2 permeating to the permeate side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. Poly(amidoamine)(PAMAM) dendrimers, candidate materials for molecular gate membranes, shows high separation performance in separation of CO_2/N_2 and CO_2/H_2. In RITE, PAMAM dendrimer/polymer hybrid membranes were developed for CO_2 separation from flue gas (CO_2/N_2) and from IGCC process (CO_2/H_2). Although dendrimer itself is viscous liquid, the dendrimer/polymer hybrid membranes are stable under pressure difference conditions, and thus suitable for practical use. The CO_2/H_2 selectivity of the membrane showed more than 30, which is required to apply membrane modules for IGCC process. From these results, a PAMAM dendrimer/polymer hybrid membrane is a

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doi:10.1016/j.egypro.2013.05.191

promising candidate for IGCC process with CO_2 capture. Based on these materials, modification of membrane materials is ongoing to improve CO_2 separation performance further.

In the development of commercial membrane modules using the PAMAM dendrimer/polymer hybrid materials, RITE, Kuraray Co., Ltd., Nitto Denko Corporation and Nippon Steel Engineering Co., Ltd. established Molecular Gate Membrane module Technology Research Association, and membrane materials, membrane modules and separation systems are being developed with collaboration in the research association.

Keywords: Poly(amidoamine) dendrimer; hybrid membrane; CO_2-selective membrane; CO_2/H_2 separation; IGCC

1. Introduction

Carbon dioxide (CO_2) capture and storage (CCS) is widely accepted as an important option for mitigating climate change [1, 2]. The cost of CO_2 capture has been reported more than 70 % of the total cost of CCS, and thus reducing the cost of CO_2 capture is a critical issue if CCS is to be implemented [3,4]. CO_2 capture by membrane is a promising technique because it is energy efficient and simple to operate [5-7]. One of the potential application for CO_2 separation membrane is an integrated gasification combined cycle (IGCC) plant with CCS. For this application, the membrane is required to have high CO_2/H_2 selectivity [8].

A number of membranes have been developed for CO_2 separation, especially for CO_2/N_2 and CO_2/CH_4 mixed gas. However, only a limited number of polymer membranes are reported to show CO_2 selectivity over H_2 [9-11]. Generally, gas permeation through polymeric membranes is explained by solution-diffusion model. With polymeric membranes, CO_2 is usually more soluble than H_2 whereas H_2 exhibits a much higher diffusivity than CO_2 because of its smaller molecular size. As a result, it has been difficult to achieve a high CO_2/H_2 selectivity. Currently, CO_2/H_2 selectivity of PEG-based materials is around 10 at 35-40 °C. However, from our simulation, it was estimated that CO_2/H_2 selectivity of more than 30 is required to apply the membrane process to IGCC process [8].

In RITE, we have been developing “molecular-gate” membrane to achieve high CO_2/H_2 selectivity of more than 30. The concept of CO_2 molecular gate membrane is shown in Fig. 1.

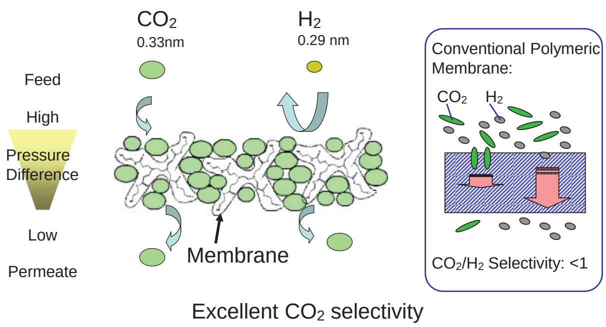


Fig. 1. Concept of CO_2 molecular gate membrane for CO_2/H_2 Separation

As shown in Fig. 1, in the case of conventional polymeric membranes, it is difficult to obtain high CO_2/H_2 selectivity, because the diffusion selectivity is favorable for H_2 which is smaller size than that of CO_2. On the other hand, in the concept of the molecular gate membrane, the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of H_2 permeating to the permeate side of the membrane is greatly limited and high concentrations of CO_2 can be obtained.

Sirkar et al. reported that Poly(amidoamine) (PAMAM) dendrimer immobilized liquid membrane (ILM) demonstrates excellent CO_2 selectivity over various gases under atmospheric pressure [12, 13]. It was suggested that PAMAM dendrimer might be used as the candidate materials for the molecular gate membranes. Possible separation mechanism of CO_2 molecular gate membrane is shown in Fig. 2.

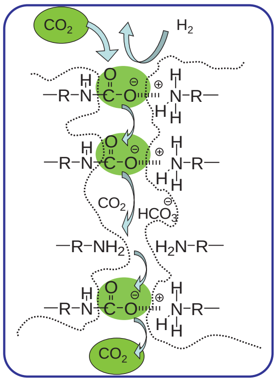


Fig. 2. Possible separation mechanism of CO_2 molecular gate membrane for CO_2/H_2 Separation

As shown in Fig. 2, CO_2 and amino group in PAMAM reacts to form carbamates which might form quasi cross-linking, which would result reducing the solubility of H_2. On the other hand, CO_2 could permeate through the membrane as bicarbonate ion or as CO_2 molecule.

The dendrimer itself has insufficient pressure durability for practical use because of the flow nature of the PAMAM dendrimer at or above room temperature. Therefore, we are developing PAMAM dendrimer/polymer hybrid membranes for the separation of CO_2/H_2 for IGCC process. So far, we developed PAMAM dendrimer/polymer hybrid membranes using crosslinked poly(ethylene glycol) (PEG) or crosslinked poly(vinyl alcohol) (PVA) as pressure-durable polymeric materials [14, 15]. In this paper, we report the development of molecular gate membrane modules for high pressure conditions for IGCC process.

2. Experimental

2.1. Gas permeation experiments

CO_2/H_2 (80/20 by vol.) gas mixture was humidified at 80-90 % relative humidity and then fed to a flat-sheet membrane cell at a flow rate of 100 ml/min. The CO_2 partial pressure at the feed side was 560 kPa. Dry He or Ar was supplied to the permeate side of the cell as a sweep gas. The operating temperature was 40 °C. The CO_2 and H_2 concentrations in both feed and permeate gas were measured by gas chromatography.

3. Results and discussion

We used poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA) as two major candidate materials for pressure-durable polymeric matrix. Example materials and reaction scheme of for PEG-matrix and PVA-marix are shown in Fig. 3.

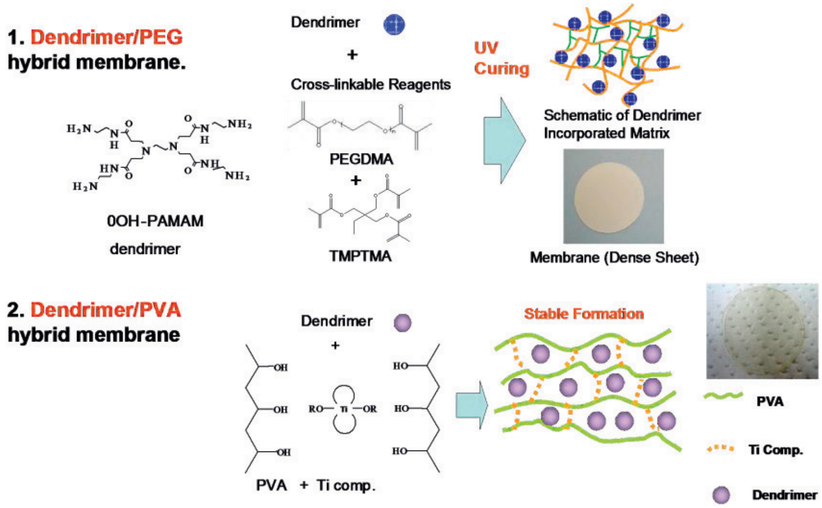


Fig. 3. Reaction scheme of PEG-type and PVA-type molecular gate membranes.

As shown in Fig. 3, dendrimer was immobilized in either crosslinked PEG matrix or crosslinked PVA matrix. As the PVA has more affinity to PAMAM dendrimer, transparent membrane can be obtained. In the case of PEG matrix, however, transparent membranes can also be obtained by tuning the materials of polymeric matrix.

Separation performance of molecular gate membranes (dense film and composite membranes) for CO_2/H_2 separation is shown in Fig. 4, along with the data of crosslinked (PEG) membranes [9].

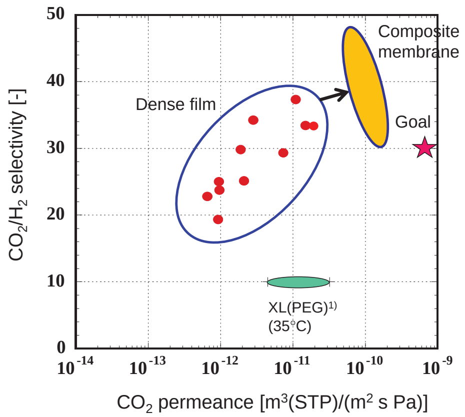


Fig. 4. Separation performance of molecular gate membranes (dense film and composite membrane) for CO_2/H_2 separation. The separation performance of crosslinked (PEG) membranes [9] is also shown in the plot.

PEG-based membranes are known as the CO_2 selective polymeric membranes, unlike many other polymeric membrane materials that show H_2 selectivity. As shown in Fig. 4, CO_2/H_2 selectivity of PEG-based membranes is around 10 at 35 °C. On the other hand, molecular gate membranes (dense film) showed CO_2/H_2 selectivity as high as 30 or more, which is required for IGCC process. The dense film was relatively thick (ca. 500 μm), and the CO_2 permeance was not high. Recently, we succeeded in producing composite membranes having thin selective layer on the porous support. In addition, we succeeded in improving membrane materials to show even higher CO_2/H_2 selectivity.

To make molecular gate membrane applicable for IGCC process, it is very important to develop the membrane modules based on PAMAM dendrimer/polymer hybrid materials. To develop membrane modules, RITE started collaboration with private membrane companies.

Generally, there are two types of membranes, i.e., (a) hollow-fiber membrane modules and (b) spiral wound membrane modules.

Molecular gate membrane module (hollow-fiber) is shown in Fig. 5.

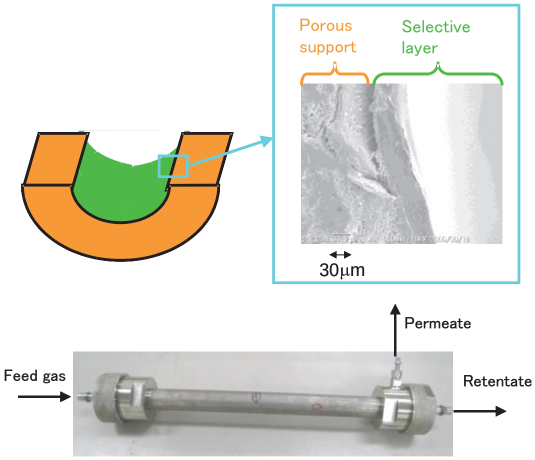
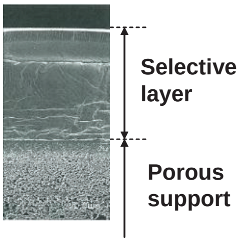


Fig. 5. Molecular gate membrane module (hollow-fiber).

As shown in Fig. 5, inner surface of hollow-fiber porous support was coated with thin selective layer composed of PAMAM dendrimer and polymeric materials.

Molecular gate membrane module (spiral-wound) is shown in Fig. 6.



(a) SEM photograph of membrane cross-section

(b) Photograph of proto-type module

Fig. 6. Molecular gate membrane module (spiral-wound).

As shown in Fig. 6, flat-sheet porous support was coated with thin selective layer composed of PAMAM dendrimer and polymeric materials. It was confirmed that the molecular gate membrane module has pressure durability as high as at least 3MPa.

4. Conclusions

PAMAM dendrimer/polymer hybrid membrane is a promising candidate for IGCC process with CO_2 capture. Based on these materials, modification of membrane materials is ongoing to improve CO_2 separation performance further.

In the development of commercial membrane modules using the PAMAM dendrimer/polymer hybrid materials, RITE, Kuraray Co., Ltd., Nitto Denko Corporation and Nippon Steel Engineering Co., Ltd. established Molecular Gate Membrane module Technology Research Association, and membrane materials, membrane modules and separation systems are being developed with collaboration in the research association.

Acknowledgements

This study is supported by Ministry of Economy, Trade and Industry, Japan (METI) and Nippon Steel Engineering Co., Ltd. The authors would like to thank Ms. Hiromi Urai, Ms. Kimiyo Kishi, Ms. Keiko Ida, Ms. Rie Sugimoto, Mr. Shigetoshi Tanaka and Ms. Sachiko Kondoh for membrane preparation, characterization and gas separation measurements.

References

[1] H. Liua, X. Liang, Strategy for promoting low-carbon technology transfer to developing countries: The case of CCS, Energy Policy 39 (2011) 3106–3116.

[2] J. Lipponen, K. Burnard, B. Beck, J. Gale, B. Pegler, The IEA CCS Technology Roadmap: One Year On, Energy Procedia 4 (2011) 5752–5761.

[3] A. Meisen, X. Shuai, Research and development issues in CO2 capture, Energ. Convers. Manage. 38 (1997) S37–S42.

[4] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer, Carbon Dioxide Capture and Storage: IPCC Special Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, 2005.

[5] P.H.M. Feron, CO2 capture: The characterisation of gas separation/removal membrane systems applied to the treatment of flue gases arising from power generation using fossil fuel. Cheltenham: IEA greenhouse gas R & D programme, 1992.

[6] V. Abertz, T. Brinkmann, M. Dijkstra, K. Ebert, D. Fritsch, K. Ohlrogge, D. Paul, K.-V. Peinemann, S. Pereira-Nunes, N. Scharnagl, M. Schossig, Developments in membrane research: from material via process design to industrial application, Adv. Eng. Mater. 8 (2006) 328–358.

[7] A. Basu, J. Akhtar, M. Rahman, M. Islam, A review of separation of gases using membrane systems, Petrol. Sci. Tech. 22 (2004) 1343–1368.

[8] R. Nagumo, et al., Techno-economic evaluation of the coal-based integrated gasification combined cycle with CO_2 capture and storage technology, Energy Procedia 1 (2009) 4089–4093.

[9] H. Lin, E.V. Wagner, B.D. Freeman, L.G. Toy, and R.P. Gupta, Science, 311 (2006) 639-642.

[10] A. Car, C. Stropnik, W. Yave, K.-V. Peinemann, J. Membr. Sci., 307 (2008) 88-95.

[11] D. Husken, T. Visser, M. Wessling, R. J. Gaymans, J. Membr. Sci., 346 (2010) 194-201.

[12] A.S. Kovvali, H. Chen, K.K. Sirkar, Dendrimer membranes: a CO_2-selective molecular gate, J. Am. Chem. Soc. 122 (2000) 7594.

[13] A.S. Kovvali, K.K. Sirkar, Dendrimer liquid membranes: CO_2 separation from gas mixtures, Ind. Eng. Chem. Res. 40 (2001) 2502.

[14] I. Taniguchi, S. Duan, S. Kazama, Y. Fujioka, Facile fabrication of a novel high performance CO_2 separation membrane: immobilization of poly(amidoamine) dendrimers in poly(ethyleneglycol) networks, J. Membr. Sci. 322 (2008) 277–280.

[15] S. Duan, I. Taniguchi, T. Kai, S. Kazama, Poly(amidoamine) dendrimer / poly(vinyl alcohol) hybrid membranes for CO_2 capture, J. Membr. Sci., in press.